CRYSTAL LATTICE DYNAMIC EFFECTS FOR SASD TYPE CRYSTALS DOPED WITH Cr^{3+} AS DETECTED BY EPR FOR $T>T_c$

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Abstract. The effect of lattice vibration on the value of the D_{zz} parameter for SASD type crystals doped with Cr^{3+} is discussed. It is shown that even for the temperatures much higher than T_c, the inclusion of short and long range correlations taking place for two inequivalent active groups $SO_4(I)(SeO_4(I))$ and $SO_4(II)(SeO_4(II))$ modify temperature behavior of the second-order spin-hamiltonian parameters expected for simple models for crystal vibrations.

1. INTRODUCTION

Sodium ammonium sulphate dihydrate (SASD) and sodium ammonium selenate dihydrate (SASeD) are ferroelectrics below 101 and 180K respectively. In our previous paper [1] we have detaily discussed the influence of the crystal lattice dynamics for the discussed crystals on the temperature dependence of D_{zz} spin-hamiltonian parameter in the near vicinity of T_c. We found that this temperature dependence is mainly determined by the effect of soft modes.

In most general terms the temperature dependence of the D_{zz} spin-hamiltonian parameter can be described by the following relation:

$$\left(\frac{\partial D_{zz}}{\partial T}\right)_P = \left(\frac{\partial D_{zz}}{\partial T}\right)_R + \left(\frac{\partial D_{zz}}{\partial T}\right)_T\left(\frac{\partial R}{\partial T}\right)_P. \qquad (1)$$

The first term on the right hand side of Eq. (1) represents the so-called explicit effect (phonon contribution) and the second term representing implicit effect (the contribution resulting from thermal expansion or contraction of the crystal). Although the separation of the contributions given by both above terms to the experimentally observed temperature dependence of $D_{zz}(T)$ is very difficult we believe, based on many experimental results and some theoretical estimation, e.g. [2,3], that vibronic effects play a dominant role in the character of the temperature dependence for the second-order spin-hamiltonian parameters.

2. EXPERIMENTAL

The single crystals of SASD and SASeD doped with Cr^{3+} were grown using the method of evaporation of saturated water solutions. The details of

the crystal growth conditions are given in [4,5]. EPR spectra were taken using a standard X-band spectrometer with the 100 kHz modulation of the steady magnetic field.

3. RESULTS

The EPR spectra of both SASD and SASeD doped with Cr^{3+} could be very well parameterized with the following spin-hamiltonian parameter:

$$H_s = \mu_B \vec{B} \vec{g} \vec{S} + \vec{S} \vec{D} \vec{S}, \qquad (2)$$

where $\vec{S}$ is the electron spin operator of the Cr^{3+} ion with S = 3/2, μ_B is the Bohr's magneton, $\vec{B}$ is the magnetic field, $\vec{g}$ is the g tensor and $\vec{D}$ the fine structure tensor. An example of the spectrum observed for SASD is shown in Fig.1.

Diagonalizing (2) and thus determining the spin-hamiltonian parameters D=3/2 D_{zz} and E=1/2(D_{xx}-D_{yy}) we decided, taking into account the experimental error (the experimental error for E is about one order larger than that for D) that the presentation of the $D_{zz}(T)$ is more representative for the temperature behaviour of the second-order spin-hamiltonian parameter than E(T).

The temperature dependences of D_{zz} for SASD:Cr^{3+} and SASeD:Cr^{3+} are presented in Figs. 2 and 3. As seen from these figures, for $T>T_c$ one

detects a linear behaviour of D_{zz} upon T but the slope changes for SASD at T=200K and for SASeD at T=288K. In Table 1 we give the results of our parameterization of linear runs of $D_{zz}(T)$ using Eq. (5).

Below, we shall discuss a possible reason explaining such behaviour.

4. INTERPRETATION

In order to describe the effect of lattice vibration on spectroscopic properties of paramagnetic dopants in crystals one usually expands the crystal field potential in a Taylor series with respect to normal coordinates Q_i:

$$V = V_0 + \sum_i (\nabla V)_0 \vec{Q}_i + \frac{1}{2} \sum_{i,j} \vec{Q}_i (\nabla^2 V)_0 \vec{Q}_j + \ldots \qquad (3)$$

In the harmonic approximation, obviously, only the third term on the right hand of (3) is considered. Due to the incoherency of different normal modes the thermal averaging procedure reduces itself to the replacement of $Q_i Q_j$ by $<Q_i^2>$. This averaging is performed over vibrational states of the ground state. Pfister *et al.* [3] found, accepting the above assumptions, that the temperature dependence of the D spin-hamiltonian parameter can be described by the following relation:
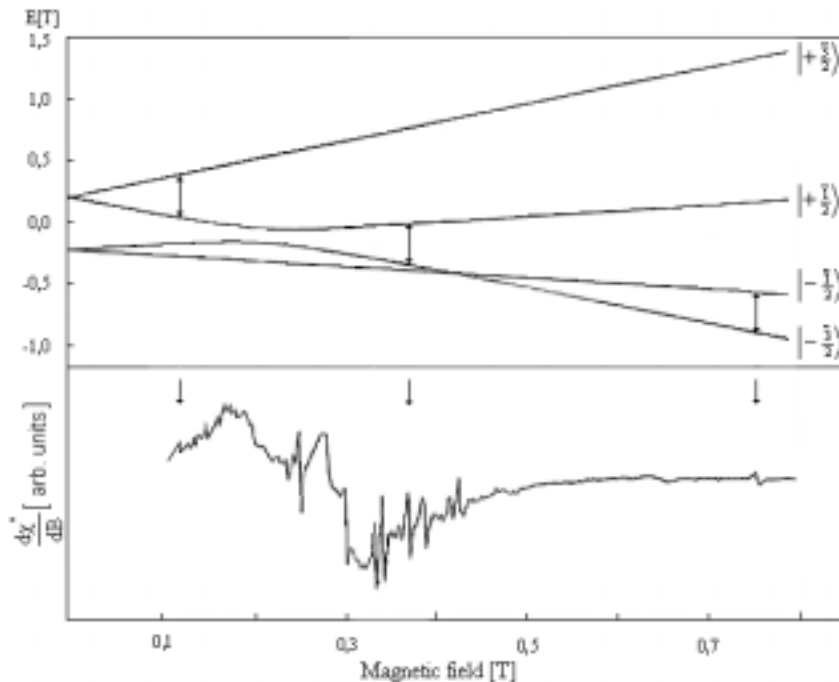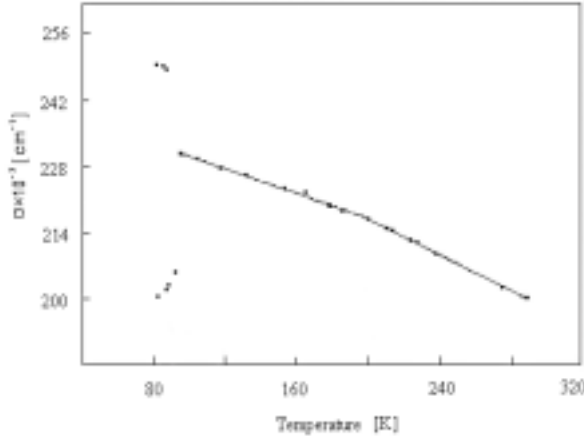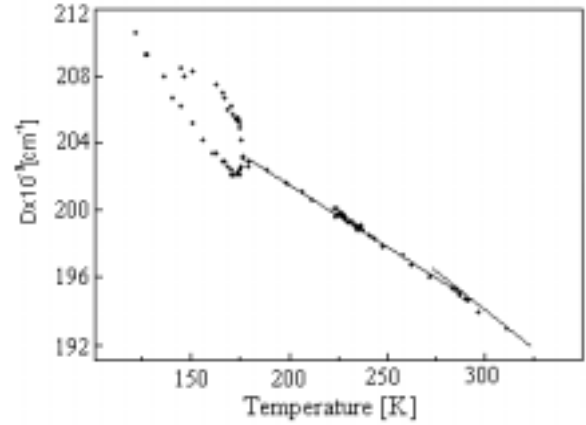

Fig. 1. The EPR spectrum of Cr^{3+} in SASD taken at room temperature for $\vec{B}$ parallel to the principal direction z.

Table 1. The values of D_0 and $-K_0^2/\omega_E$ for SASD and SASeD doped with Cr³⁺.

| $D_0 \cdot 10^{-3}$ [cm⁻¹] | | | | $-K_0^2/\omega_E \cdot 10^{-3}$ [cm⁻¹·s] | | | |
| SASeD:Cr³⁺ | | SASeD:Cr³⁺ | | SASeD:Cr³⁺ | | SASeD:Cr³⁺ | |
T [K]	T [K]	T [K]	T [K]	T [K]	T [K]	T [K]	T [K]
176÷275	275÷315	176÷275	275÷315	176÷275	275÷315	96÷200	200÷290
209	213	246	239	22,86	22,41	12,36	18,56

Fig. 2. Temperature dependence of D_{zz} parameter for SASD doped with Cr³⁺.

Fig. 3. Temperature dependence of D_{zz} parameter for SASeD doped with Cr³⁺.

$$D(T) = D_0 + D_0 \sum_{j=1}^{p} \frac{\left(\omega_j^2 - \omega_j'^2\right)\hbar \, \mathrm{ctg}h \frac{\hbar\omega_j}{2kT}}{4\omega_j \Delta E} + \frac{D_0}{2B_2^0(0)} \sum_{j=1}^{p} \frac{\partial B_2^0}{\partial Q_j^2} \frac{\hbar}{2m\omega_j} \mathrm{ctg}h \frac{\hbar\omega_j}{2kT}. \tag{4}$$

D_0 is the so-called "rigid lattice" value of D and DE is, in our case, the energy difference between the first excited state ⁴P and the ground state ⁴F estimated to be about 14000 cm⁻¹. Therefore, it may be concluded that the second term of (4) contributes little to the temperature dependence of the D spin-hamiltonian parameter especially when one considers optic modes.

Taking into account the above considerations we come to the conclusion that the most convenient parameterization scheme should be this resulting from Einstein model for lattice vibrations

$$D(T) = D_0 + K_2^0 \, \mathrm{ctg}h \frac{\hbar\omega_E}{2kT}. \tag{5}$$

Here, K_2^0 is a constant describing the magnitude of spin-phonon interactions and its meaning can easily be inferred considering the third term of Eq. (6).

The results of the parameterization using Eq. (5) are presented in Table 1. SASD and SASeD have the same crystal structure but their crystal dynamics should somehow differ because of the difference in atomic masses between S (μ_A=32.066) and Se (μ_A=78.96). In the simple harmonic approximation and assuming that K_2^0 is the same for both crystals one should expect that the value of ω_E(SASD)/ω_E(SASeD) should be the same as the value of $\sqrt{\mu_S / \mu_{Se}}$. This relation, taking into account the data given in Table 1 is, however, is not fulfilled. For example, for high temperature region we find that ω_E(SASD)/ω_E(SASeD) is 0.83 whereas the value of $\sqrt{\mu_S / \mu_{Se}}$ is 0.63. Even when we take into account the experimental error, the difference between these two above given values is too large. Thus, other effects contributing to lattice dynamics should be expected to take place.

Over the last few years we have studied both experimentally and theoretically the ferroelectric properties of SASD type single crystals [6] and found that these properties and other anomalies detected are mainly determined by the dynamical behaviour of two active groups (SO$_4$(I) and SO$_4$(II) for SASD and SeO$_4$(I) and SeO$_4$(II) for SASeD). Two types of interactions between these groups were found: long range one is described by $\tilde{J}$ and short range one is described by $\tilde{K}$ (see [6]). The coexistence of these interactions allowed us the explanation of the existence of some anomalies observed previously in dielectric, thermal, EPR and neutron scattering experiments [7].

Our recent studies on the role of soft modes in the vicinity of T_c [1] allowed us to extend the theoretical considerations to include the contribution played by bounded phonon – dipole excitations. As given in [1] in this case the pseudospin - lattice hamiltonian for the system investigated has the following form:

$$H = \sum_{i,n} \Lambda_n x_i^{nn} + \sum_{k,a} \hbar\omega_a(\vec{k})\beta_{ka}^+\beta_{ka} +$$

$$\sum_{i,f,k,a\,m,n} \sum \alpha_{mn}^{(f)} X_i^{mn}\tau_{af} e^{i\vec{k}\vec{R}_i}\left(\beta_{ka} + \beta_{-ka}^+\right). \tag{6}$$

Using the method of double – time Green functions one can obtain the following dispersion relation:

$$\left(E^2 - \hbar^2\omega_1^2\right)\left(E - \Lambda_{mn}\right) =$$

$$128\hbar\omega_1\tau_{11}^2 \frac{\left(\Delta + J_2\xi\right)^2\left(\Lambda_m + \Lambda_n\right)^2}{\eta_m^2\eta_n^2} <X^{nm} - X^{nn}>. \tag{7}$$

The exact meaning of all symbols appearing in [3,4] is explained in [1]. For the context of this paper it is sufficient to notice that Λ_{mn}, Λ_m, and Λ_n are functions of two parameters $\tilde{J}$ and $\tilde{K}$.

When detailed calculations are carried out including the values of $\tilde{J}$ and $\tilde{K}$, which were previously determined [6] one comes to the conclusion that they increase phonon fequencies for both SASD and SASeD but not in the same way. For SASeD the increase in the value of ω_E is greater than for SASD so that the ratio ω_E(SASD)/ω_E(SASeD) is indeed close to 0.63 as found experimentally.

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